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Development of quantitative analysis method for tritium using by hydrophobic platinum catalyst

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ABSTRACT

Various methods of tritium measurement have been applied depending on a chemical form of tritium. A method combined oxidation catalyst and water bubblers has been used as one of the most quantitative analysis methods for gaseous tritium. The major technical shortcoming with the conventional methods is the lowering of quantitative accuracy caused by adsorption of produced tritiated vapor on hydrophilic oxidation catalyst. Then, we developed an organic-based hydrophobic platinum catalyst. The catalyst enhanced its hydrophobicity to prevent absorption of water vapor on catalyst surface. In order to ensure to oxidize tritium, we additionally devised 1) the particle size of the catalyst made small to be around 1 mmϕ and 2) intentional addition of hydrogen. As the result of experimental verification of the proposed method, we succeeded to achieve the high accuracy of more than 99.9% in the quantitative measurement of tritium. The developed tritium measurement system is applicable widely for various tritium measurements, estimation of tritium generation rate at TBM, tritium behavior in various materials and so on.

1. Introduction

Various methods of tritium measurement are applied corresponding to the concentration, the chemical form, the state and environment. Gaseous tritium measurement includes a method to measure ionization current generated by beta rays of tritium such as ionization chamber and proportional counters and also a method to measure radioactivity of a liquid sample collected tritium by liquid scintillation counting. A liquid scintillation counter is superior in measuring low concentration of tritium present in environment [1–3]. Then, a method combined oxidation catalyst and a trap such as an adsorbent, a cold trap or a water bubbler is used as one of the most quantitative analysis methods for tritium [1–4]. The method is not suitable for real-time monitoring but for measurement of tritium in a wide range of concentrations. The method also enables to distinguish the chemical forms between gaseous tritium and tritiated water vapor [2, 3]. In the method tritium is oxidized by oxidation catalyst. Then oxidized tritium is collected in a water bubbler and tritium collected in bubblers is analyzed by liquid scintillation counting. Copper oxide and hydrophilic platinum catalyst are generally used as tritium oxidation catalyst in a conventional method [4–6]. However, the major technical shortcoming with the conventional methods is the lowering of quantitative accuracy caused by absorption of produced tritiated vapor on oxidation catalyst having hydrophilic property. The adsorption leads to incorrect mass balance of tritium due to adsorption of oxidized tritium on oxidation catalyst and caused misunderstanding of tritium behavior due to the delayed desorption of oxidized tritium from oxidation catalyst [6]. In order to respond the strong need of tritium measurement with high accuracy to understand the transient behavior of tritium released from tritium breeding material, the absorption of produced tritiated vapor on oxidation catalyst should be avoided as much as technically possible.

For this purpose, we developed an organic-based hydrophobic platinum catalyst to be applied for quantitative tritium measurement system. In the present study, we devised a high quantitative tritium measurement system and demonstrated the performance of the measurement system.

2. Experimental

2.1. Devisal for quantitative tritium measurement system

A quantitative tritium measurement system was proposed. It composed of a catalytic reactor packed with hydrophobic platinum catalyst and two water bubblers connected in series. In the catalytic reactor, tritium in air was completely oxidized to be tritiated

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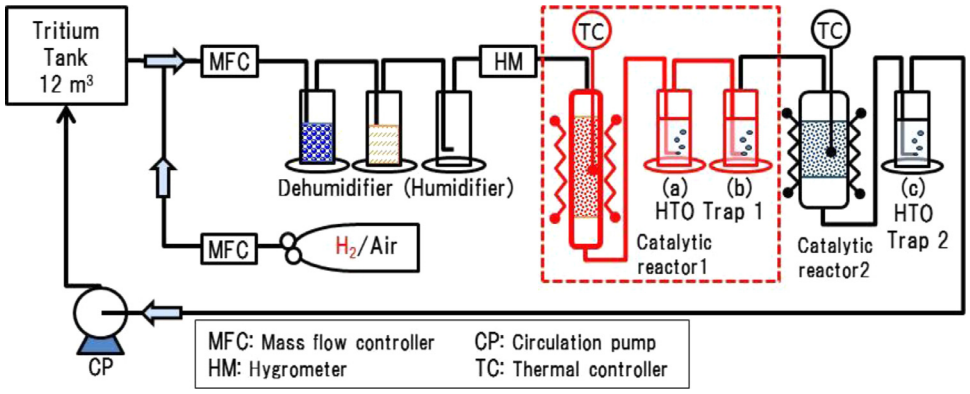

Fig. 1. Experimental apparatus to determine the performance of tritium oxidation. MFC: mass flow controller; HM: hygrometer; TC: temperature controller and CP: circulation pump.

water vapor (HTO). The water bubblers acted as the selective trap of HTO from air. In order to avoid retention of oxidized tritium by adsorption, we developed an organic-based hydrophobic platinum catalyst. The catalyst enhanced its hydrophobicity to prevent absorption of oxidized tritium on catalyst surface. In addition, the hydrophobic platinum catalyst can maintain the activity in the presence of water vapor due to its hydrophobicity, whereas it is well known that hydrophilic platinum catalyst considerably lowers the activity due to the covering of active sites by water molecules. In order to oxidize tritium completely in the reactor, we carefully selected the particle size of the catalyst. This is because an increase in contact surface area per packed volume enhances the efficiency of reaction in a case the diffusion in pores is the rate controlling step. It has been well demonstrated the efficiency of reaction has a dependency on hydrogen concentration. Smaller hydrogen concentration causes lower efficiency of reaction. The concentration of tritium to be oxidized is generally below the natural hydrogen content in air. In order to enhance the efficiency of reaction and to downscale a catalytic reactor, initial addition of hydrogen was proposed to oxidize tritium efficiently.

2.2. Performance test

Fig. 1 schematically illustrates the catalytic reactor flow system to demonstrate the performance of the proposed quantitative tritium measurement system. In the catalytic reactor flow system, the quantitative tritium measurement system we proposed is boxed by a dashed line. The catalytic reactor flow system has two catalytic reactors. The first catalytic reactor is the core of the quantitative tritium measurement system and the second catalytic reactor is to oxidize the tritium unreacted in the first catalytic reactor. The catalyst packed in the first reactor was a hydrophobic platinum catalyst which is supporting Pt directly on styrene diviylbenzene copolymer (Pt/SDBC). The catalyst used in the tests was commercially named Kogel catalyst, test-manufactured by SHOKO Co., Ltd., Japan [7]. The Pt/SDBC catalyst was 1.0 wt% Pt/SDB particles with the diameter of 1 mmϕ. In order to uniform temperature distribution in the catalytic reactor by heating from the outside surface of the reactor, the catalytic reactor was a slender shape with the inner diameter and length of 15.8 mm and 500 mm, respectively. The volume of the Pt/SDBC catalyst packed in the catalytic reactor was 94 cm^3 to oxidize tritium completely. In the second reactor, Pt/Al_2O_3 catalyst was packed to oxidize HT unreacted in the first reactor completely. The Pt/Al_2O_3 catalyst was 0.5 wt% Pt/Al_2O_3 pellets manufactured by N. E. Chemcat Corporation, Japan. The inner diameter and length of the second catalytic reactor were 56.5 mm and 150 mm, respectively. The volume of the Pt/Al_2O_3 catalyst packed in the catalytic reactor was 200 cm^3. Both catalytic reactors were thermally insulated. The temperature of catalyst layer was controlled by a temperature controller. The temperature of catalyst layer was monitored with a thermocouple. Careful attention was paid to the low thermal stability of Pt/SDBC catalyst due to polymeric substrate. The maximum temperature of Pt/SDBC catalyst layer was 100 °C. The temperature of Pt/Al_2O_3 catalyst layer was kept at 200 °C. The Pt/Al_2O_3 catalyst layer was continually washed out by wet air from HTO trap 1, then tritium adsorption on the surface of Pt/Al_2O_3 catalyst was kept to be negligibly small.

A mixture gas of tritium balanced in air was supplied from a tank of 12 m^3 to the catalytic reactor flow system. The system was capable of flow rates of 100–1500 cm^3/min controlled with a mass flow controller (8500MC, KOFLOC, Japan). The concentration of the tritium in air was approximately 370 Bq/cm^3. The concentration of water vapor in a mixture gas supplied was controlled with/without a humidifier (a wet/dry condition) after water vapor was removed by two dehumidifiers packed with silica gel beads and molecular sieves 5A pellets, respectively. The hydrogen was intentionally added for the hydrogen concentration of the mixture gas to be a desired value (0–5000 ppm). The mixture gas passed through the first catalytic reactor packed with Pt/SDBC catalyst. Gaseous tritium (HT) converted to the oxide by the Pt/SDBC catalyst and collected by the water bubblers (a) and (b) of the HTO Trap 1 as shown in Fig. 1. Gaseous tritium unreacted in the first catalytic reactor fed into the second reactor packed with Pt/Al_2O_3 catalyst and was completely oxidized by the Pt/Al_2O_3 catalyst, the oxidized tritium was collected by the water bubbler (c) of the HTO Trap 2. The tritiated water sample was taken from the HTO Trap 1 and Trap 2 by pipetting. The weight of the sample was measured taking variations in the amount of tritiated water by pipetting into consideration. The tritium activity in the HTO Trap 1 and Trap 2 was measured by a liquid scintillation counter (LSC6100, Aloka Co., Ltd., Japan). The water bubbler used to enhance efficiency of tritiated vapor trapping was a gas washing bottle that could contain a volume of 500 ml with a cylindrical glass filter with the pore size of 100–160 mm manufactured by SIBATA SCIENTIFIC TECHNOLOGY LTD. When the bubbler was filled with water of 200 ml at room temperature, the height to water surface from bottom of the filter was 37 mm.

In order to establish the quantitative tritium measurement system, tritium should be completely oxidized in the catalytic reactor and produced tritiated vapor should be completely trapped in the HTO traps. In evaluation of accuracy of proposed quantitative tritium measurement system, the system consists of two subsystems which are catalytic reactor packed with hydrophobic catalyst and water bubblers connected in series. Hence, the accuracy of proposed quantitative tritium measurement system can be assessed

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by multiplication of conversion rate of tritium and efficiency of tritiated vapor trapping in the bubblers.

Performance of the quantitative tritium measurement system is determined by conversion rate of tritium in the first catalytic reactor and efficiency of tritiated vapor trapping in the HTO trap 1. The conversion rate of tritium, CR_T, by the first catalytic reactor is determined from the following equation;

$$CR_T = \frac{A_{T,a} + A_{T,b}}{A_{T,a} + A_{T,b} + A_{T,c}}, \quad (1)$$

where $A_{T,a}$, $A_{T,b}$ and $A_{T,c}$ are tritium activity in water of the bubbler (a), (b) and (c), respectively. The efficiency of tritiated vapor trapping by a single water bubbler, EC_{HTO}, is determined from the following equation;

$$EC_{HTO} = \frac{A_{T,a}}{A_{T,a} + A_{T,b}}. \quad (2)$$

When two water bubblers connected in series are used, the efficiency of tritiated vapor trapping by a two water bubbler connected in series, $[EC_{HTO}]^2$, is expressed as follows:

$$[EC_{HTO}]^2 = (1 + (1 - EC_{HTO}))EC_{HTO}, \quad (3)$$

where the subscript of 2 in left side shows a number of bubblers. Accuracy of performance of the proposed quantitative tritium measurement system is assessed by the multiplication of CR_T and $[EC_{HTO}]^2$.

3. Results and discussion

3.1. Conversion rate of tritium by the catalytic reactor packed with hydrophobic Pt catalyst

Fig. 2 show the effect of conversion rate of tritium in the hydrophobic catalyst layer on temperature of catalyst. The conversion rate is larger than 99% in the condition that the flow rate is 1000 cm^3/min, hydrogen concentration at 1000 ppm by the addition from the gas cylinder and the temperature range of 50–100 °C. Especially above 70 °C the conversion rate increased to 99.9%. From the result, we found that tritium can be completely oxidized at a moderate temperature below 100 °C when the hydrophobic platinum catalyst is applied to the oxidation catalyst. Tritium has been conventionally oxidized over a typical catalyst such as hydrophilic Pt/Al_2O_3 or copper oxide. The temperature of copper oxide layer for tritium oxidation has been set to be around 500 °C for an example. The permeation of tritium from the reactor surface is a

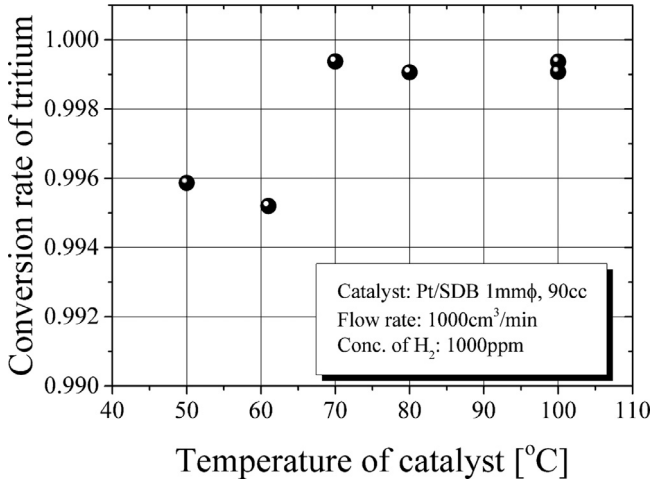

Fig. 2. Effect of temperature on the conversion rates of tritium on the hydrophobic catalyst.

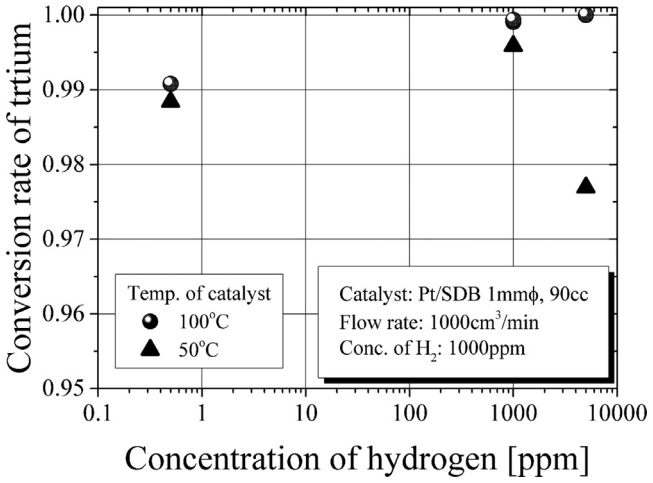

Fig. 3. Effect of hydrogen addition on the conversion rates of tritium on the hydrophobic catalyst.

technical issue of the tritium measurement system for the TBM where a gas accompanied with a large amount of tritium should be quantitatively analyzed with a tritium measurement system. This moderate temperature is a technical advantage of this system since the permeation of tritium from the reactor can be inhibited.

Fig. 3 shows the effect of hydrogen concentration on the conversion rate of tritium for the hydrophobic catalyst. The hydrogen concentration without hydrogen addition was determined as 0.5 ppm of the natural hydrogen content in air. Then tritium concentration was much smaller than that of the natural hydrogen content in air. It is well demonstrated the conversion rate for hydrogen depends on the hydrogen concentration. Smaller hydrogen concentration causes lower efficiency of reaction. It is required for a tritium measurement system to oxidize tritium completely with the careful consideration that the oxidation of a tracer level of hydrogen concentration is originally very difficult. Hence, the intentional addition of hydrogen to a gas accompanied with tritium is an effective way to enhance the efficiency of reaction. When the intentional hydrogen addition is applied, the effect of moisture produced by oxidation reaction on the efficiency of reaction needs to check carefully since the platinum itself shows the hydrophilic property even though the adsorption of moisture on substrate and formation of water layer to cover the active sites are completely prevented by strong hydrophobic property of the substrate. The hydrophilic property of platinum is notably revealed at a temperature below 50 °C. The drop of 50 °C at 5000 ppm of hydrogen concentration results from the partial inertness of active sites by the adsorption of moisture on platinum.

Fig. 4 shows the effect of moisture concentration in feed gas on the conversion rate of tritium for the hydrophobic catalyst. The drop of the dry condition at 40 °C results from the similar reason as mentioned above. Under the wet condition, the hydrophilic property of platinum dominates the efficiency of reaction. The partial inertness of active sites by the adsorption of moisture on platinum increases with a decrease in temperature. The temperature above 95 °C is a criterion for negligible affection of hydrophilic property of platinum to the efficiency of reaction. It should be noted that intentional addition of moisture has a technical advantage to prevent retention of tritiated moisture on platinum surface by hydrogen isotopic exchange between moisture in air and tritiated moisture on platinum surface. Under the dry condition, our experimental verification indicates the residual tritium amount on platinum surface was negligibly small. However at a low temperature below 50 °C the amount reached 3.0% of total tritium amount fed into the reactor.

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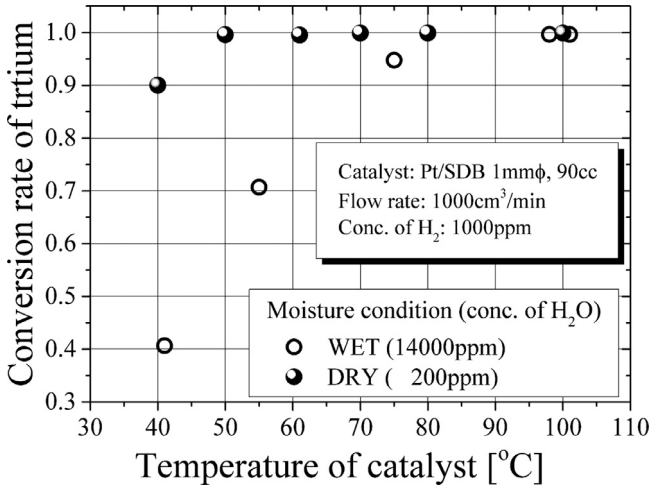

Fig. 4. Effect of moisture condition on hydrogen addition on the conversion rates of tritium on the hydrophobic catalyst.

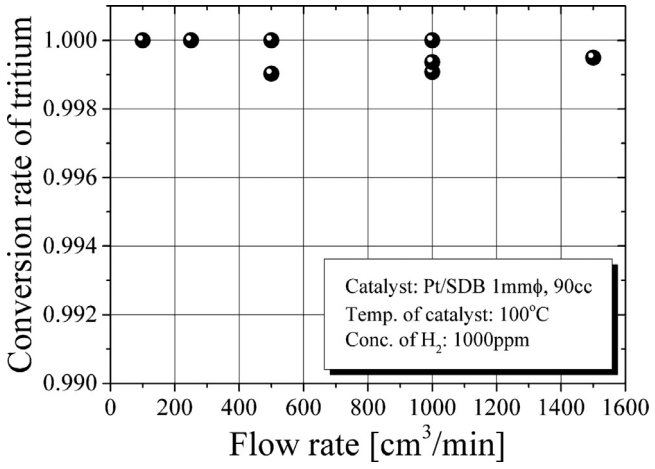

Fig. 5. Effect of gas flow rates on the conversion rates of tritium on the hydrophobic catalyst.

Fig. 5 shows the effect of gas flow rate on the conversion rate of tritium for the hydrophobic catalyst. In a wide range of gas flow rates, the conversion rate was kept more than 99%. A narrow reactor prevents the wide thermal profile when the reactor is heated from the outer surface. In addition, it brings larger superficial velocity. It is generally known that the mass transfer resistance of gas laminar film becomes dominant at a smaller superficial velocity and the resistance significantly lowers the efficiency of reaction. It is true that a narrow reactor packed with granular catalysts enhances the pressure drop. Therefore, the shape of reactor should be determined taking the pressure drop into consideration. The acceptable level will be determined from the design of the apparatus where the proposed tritium measurement system is installed.

In evaluation of accuracy of proposed quantitative tritium measurement system, uncertainty in measurement has been carefully considered. In order to evaluate the uncertainty of calculated conversion rate of tritium based on Eq. (1), we have to consider the errors in gas flow rate control, in measurement of sample weight, in tritium activity counting, in efficiency of collection of tritiated water vapor. Assessment of uncertainty in measurement was conducted according to the "Guide to the Expression of Uncertainty in Measurement" published by the initiative of the International Committee of Weights and Measures. [8]. Among them, uncertainty in tritium activity counting by a liquid scintillation counter

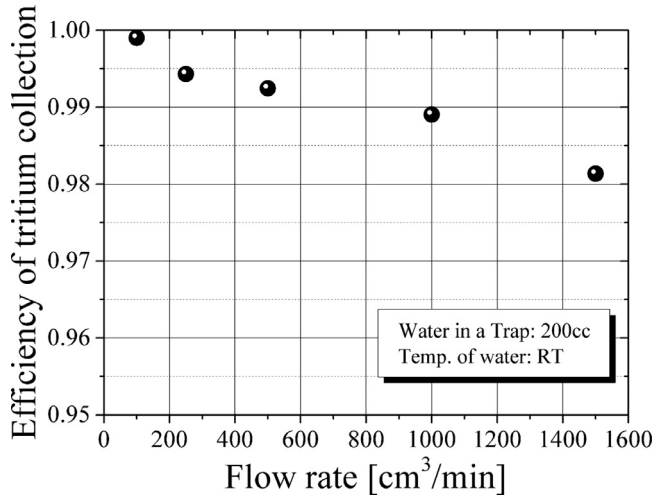

Fig. 6. Effect of gas flow rate on efficiency of tritiated vapor trapping by a HTO trap of a single water bubbler.

dominants the accuracy of proposed quantitative tritium measurement system. The uncertainty in evaluation of $A_{T,a}$ is 0.49% in a range of tritium activity 10^6–10^5 Bq/cc. The uncertainties in evaluation of $A_{T,b}$ and $A_{T,c}$ are 6.7% in a range of tritium activity 10^3–10^0 Bq/cc. The calculated accuracy for 99.9% is $99.9 \pm 6.8 \times 10^{-3}$%.

3.2. Efficiency of tritiated vapor trapping in the bubblers connected in series

Efficiency of tritiated vapor trapping in a single water bubbler can be defined as Eq. (2). It is true that the efficiency depends on the gas flow rate, volume of water in the bubbler, a type and shape of glass porous filter of the bubbler and so on. Fig. 6 shows effect of gas flow rate on efficiency of tritiated vapor trapping in a single water bubbler in the tested condition. The efficiency of tritiated vapor trapping in a single water bubbler decreased with an increase in gas flow rate. It was no less than 98.1% in a range of tested gas flow rate. Although the efficiency of tritiated vapor trapping in a single water bubbler at the flow rate of 1500 cm^3/min was 98.1%, tritiated vapor passed through the water bubber (a) due to a miss of trapping and evaporation of water in the water bubbler was trapped in the water bubbler (b). Concerning on accuracy, uncertainty in evaluating the efficiency of tritiated vapor trapping in a bubbler can be equated with uncertainty in tritium activity counting with a liquid scintillation counter since the subsystem was operated in a straight-through mode. The uncertainty in evaluation of $A_{T,a}$ and $A_{T,b}$ depends on tritium activity in a LSC sample. The uncertainty in evaluation of $A_{T,a}$ is 0.49% in a range of tritium activity 10^6–10^5 Bq/cc. The uncertainty in evaluation of $A_{T,b}$ is 6.7% in a range of tritium activity 10^3–10^0 Bq/cc. In the light of definition of the efficiency of tritiated vapor trapping in a bubbler, uncertainty in evaluation of $A_{T,b}$ influences negligibly the assessed efficiency of 98.1% since the value of $A_{T,b}$ is much smaller than that of $A_{T,a}$. Hence, this evaluation results in more than 99.96% of the efficiency of tritiated vapor trapping in the bubblers connected in series calculated from Eq. (3). The calculated accuracy for 99.96% is $99.96 \pm 6.81 \times 10^{-4}$%.

3.3. Accuracy of proposed quantitative tritium measurement system

Performance of the quantitative tritium measurement system is determined by efficiency of tritiated vapor trapping of the HTO traps and conversion rate of tritium in the catalytic reactor. We evaluated accuracy of conversion rates of tritium and efficiency

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of tritiated water vapor trapping as mentioned above. Accuracy of performance of the quantitative tritium measurement system is possible to be assessed by the multiplication of the conversion rate and the efficiency of tritiated water trapping. The accuracy for 99.9% of conversion rate and 99.96% of efficiency tritiated vapor tapping in the tritium measurement system is evaluated $99.86\% \pm 6.89 \times 10^{-3}\%$ in the test condition. Especially, the accuracy is possible to be increased more than 99.9% in the appropriate condition such as temperature of the catalyst of 100 °C.

Conclusions

We developed an organic-based hydrophobic platinum catalyst to be applied for a quantitative measurement system of tritium. The catalyst enhanced its hydrophobicity to prevent adsorption of water vapor on catalyst surface. In order to ensure to oxidize tritium, we additionally devised 1) the particle size of the catalyst made small to be around 1 mmϕ and 2) intentional addition of hydrogen. As the result of experimental verification of the proposed method, we succeeded to achieve the high accuracy of more than 99.9% in the quantitative measurement system of tritium. The developed tritium measurement system is applicable widely for various tritium measurements, estimation of tritium generation rate at TBM, tritium behavior in various materials, atmospheric tritium sampling and so on.

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